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MATCHING FLUID PROPERTIES WITH PROJECTED LUBRICANT REQUIREMENTS

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AIR FORCE MATERIALS LABORATORY
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PROVIDES CURRENT [AT THE TIME] APPROACHES BEING FOLLOWED IN THE DEVELOPMENT OF LIQUID LUBRICANTS TO MEET THE PROJECTED REQUIREMENTS OF ADVANCE SYSTEMS. DISCUSSES THE TECHNIQUES USED BY THE FLUID AND LUBRICANT MATERIALS BRANCH IN EVALUATING CANDIDATE FLUIDS AND THE SUBSEQUENT SIGNIFICANCE OF ACCUMLATED DATA.

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FOREWORD

This report was prepared by the Fluid and Lubricant Materials Branch of the Nonmetallic Materials Division. The work was initiated under Project Nr. 3044, "Aerospase Lubricants", Task Nr. 304405, "Liquid Lubricants". The work was administered under the Air Force Materials Laboratory, Deputy Commander/Research & Engineering, Aeronautical Systems Division, with Frank J. Harsacky acting as project engineer.

ABSTRACT

Provides current approaches being followed in the development of liquid lubricants to meet the projected requirements of advanced systems. Discusses the techniques used by the Fluid and Lubricant Materials Branch in evaluated candidate fluids and the subsequent significance of accumulated data.

This report has been reviewed and is approved.

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INTRODUCTION

The severe environments associated with aerospace systems preclude the use of readily available commercial liquid lubricants, therefore candidate lubricants for these advanced systems must be selected from new or improved fluids resulting from research and development programs. A number of questions arise concerning the selection of candidate lubricants: Where and how are these selections made? What properties of a material are most pertinent to its selection? How can a research chemist determine whether or not a newly synthesized fluid is of interest to the Air Force as an advanced lubricant? Where should samples be sent and what quantities are required? The purpose of this paper is to provide some answers to these questions, and in doing so, to discuss current approaches being followed in the development of liquid lubricants to meet the projected requirements of advanced systems.

LIQUID LUBRICANTS DEVELOPMENT

Within the Nonmetallic Materials Laboratory of Materials Central, the Fuels and Lubricants Branch has the major responsibility for selection and development of lubricants to meet future needs. It is to this Branch, therefore that samples of potential fluids should be submitted. The type, amount, and stage of development of each material will generally determine what happens to a sample fluid. For example, if a fluid is available in multi-gallon quantities and physical and chemical data and deposition tests indicate it to be a promising candidate for an advanced gas turbine oil, it may be scheduled for high temperature bearing rig tests without any other actual testing in this laboratory. Promising high temperature hydraulic fluids may be considered for pump tests, if available in large quantities (15 gals). Most new materials however, are available in very limited quantities and, being new, have undergone little or no evaluation as potential liquid lubricants.

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It is this group of materials that are of primary concern in this paper. As these new materials become available, they undergo a series of laboratory tests to provide property data which can be used as a basis for matching the fluids with various advanced system requirements. In this "matching" process a number of challenges must be met. Foremost among these are the limitations in the number and the quantity of fluids available as potential lubricants for advanced systems.

Today, the choice of suitable materials is considerably more restricted than prior to World War II when petroleum, with its broad spectrum of properties, provided a wide variety of lubricants to meet most requirements. Present and future environments rule out the use of petroleum in most advanced systems. The major exception is the use of super-refined mineral oils in advanced hydraulic systems. In effect, the laboratory flask has replaced the oil barrel as the prime source of materials.

Since most of the new fluids are provided by synthetic research, preliminary samples are usually one pint or less in quantity. Obviously, extensive property studies cannot be made on these materials, even with scaled-down test procedures. In this early stage, large scale performance tests requiring gallon quantities of material are impractical due to the time and expense involved in synthesis. Quite often, therefore, the immediate direction of further research must be based on a minimum amount of data.

Although the suitable materials are reduced in number, those few that are available cover a broad range of chemical types, including inorganic as well as organic compounds. Workers conducting property studies must acquire competence in all of the divergent chemical classes involved in order to effectively evaluate the merits of each material. Test procedures and apparatus may also require modification to adapt them to each of the chemical classes of materials, particularly at the higher temperatures of the future.

The study of these newer materials is centered in the Liquid Lubricants Development Group of the Fuels and Lubricants Branch. Through this group, both in-house and contractual efforts are expended in characterizing base fluids, additives, and small-scale formulations. The various fluids are categorized on the basis of initial property data. In general, if a base fluid (or formulation) exhibits good thermal and oxidative stability as well as fluid range, it may undergo development as an advanced gas turbine engine oil. If a fluid has good thermal stability and broad fluid range, but lacks the desired oxidative stability for use as an engine oil, it may be considered as a candidate for an advanced hydraulic fluid. Hydraulic systems exclude oxygen (air) and therefore do not require oils with as high a level of oxidation stability as an engine. A candidate fluid for high temperature lubricating greases must have very low volatility and have long-term thermal and oxidative stability.

In each of the application categories mentioned above, there are certain requirements of primary importance which must be met by the candidate fluid. In a fluid which meets these requirements it is generally necessary to compromise one or more of the requirements of secondary importance since none of the present materials will meet all requirements in all respects.

In order to discuss in more detail the development process which sample fluids undergo, the current program for development of advanced gas turbine oils will serve as an example.

DEVELOPMENT OF ADVANCED GAS TURBINE ENGINE OILS

The prime target in this program is the development of an advanced gas turbine oil capable of operation at bulk oil temperatures of at least 500°F, while having the necessary fluidity at temperatures as low as -40°F. This oil must also have the thermal and oxidative stability necessary to prevent formation of deleterious decomposition products while exposed to the high bulk oil temperature, hot spots, and the oxidizing environment present in gas turbine engines. Finally, the oil must be a good lubricant, i.e., it should prevent excessive wear and have the ability to carry the applied loads encountered. Of course, many other properties such as foaming, compatibility, volatility, etc., must also be considered.

The overall Air Force program for the evolution of a new gas turbine oil is shown in Figure 1.

FIGURE 1

STEP-WISE EVOLUTION OF A GAS TURBINE OIL

Step:	1		2		3		4		5
	Research On New Compounds	⟶ / ⟵ - - -	Property and Formulation Studies	⟶ / ⟵ - - -	Simulated Component Studies	⟶ / ⟵ - - -	Static Engine Tests	⟶ / ⟵ - - -	In-Flight Engines

This sequence was generally followed in past development programs and is being followed in the current program. The solid arrows show the progression of the candidate oil, and its data from the research laboratory to the operational engine. The broken arrows represent the backfeed of information.

Step 1 represents the laboratories that are the source of new high temperature liquid compounds. These sources include the in-house laboratories of Materials Central, laboratories under contract to the Air Force, and other industrial research laboratories. Chemical compounds currently under study at these sources include phospho-nitriles, perfluoroalkyls and aromatics, pyrazines, triazines, aryl esters, and polyphenyl ethers.

Step 2 in this sequence is the phase in which the Liquid Lubricants Development Group operates. It is here that the new liquid materials are received for initial property studies as base or "neat" fluids. The most promising base stocks are then formulated with various combinations of additives to determine the optimum formulation.

Data obtained in Step 2 are not only used to select candidate formulations for further evaluation in Step 3, but are also fed back to step 1 for guidance in further research.

The formulations which enter Step 3 must first be obtained in larger quantities. Often, this involves scale-up of low yield synthesis procedures and subsequent re-evaluation of the larger sample to assure retention of all significant properties.

In Step 3, the candidate lubricant is called on to operate in dynamic systems, in which many properties of the lubricant are being evaluated at the same time. These simulated components include high temperature bearing rigs, deposition rigs and gear rigs. The lubricant is subjected to combinations of high temperature oxidizing environment, high speeds, and high loads. It is in intimate contact with large areas of various metals. Collectively, these tests give a measure of the lubricant with regard to (1) its resistance to massive decomposition and formation of harmful deposits, (2) its anti-wear and load-carrying properties, and (3) its compatibility with the materials which it contacts.

Despite all of these preliminary studies, the suitability of the lubricant cannot be determined without extensive static engine testing, followed by actual flight tests. As the candidate lubricant proceeds from the laboratory evaluation to the engine tests, complexity and costs sky-rocket, therefore it is obvious that if rapid and efficient progress is to be made, the initial property evaluations (in step 2) must produce data that are selective and are closely related to the actual demands of an advanced engine. A general discussion of these evaluation procedures follows.

INITIAL PROPERTY AND FORMULATION STUDIES All samples of potential lubricating fluids submitted to the Liquid Lubricants Development Group undergo a series of initial property studies, first as base fluids, followed by formulation with additives. The properties of primary interest are listed in Figure 2. Generally the laboratory submitting the sample fluid has already conducted screening tests on the material.

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If these data, and the test methods are provided with the sample, a saving in time and material may be realized during this initial property study.

FIGURE 2

Oxidation-Corrosion	Pour Point
Thermal Stability	Flash Fire
Viscosity-temperature	Anti-Wear
Volatility	Hydrolytic Stability

The principal evaluation procedure which candidate fluids undergo is the oxidation-corrosion test. A standardized "micro" procedure has been developed which requires only 20 ml of the sample material for each determination. With five different metal specimens immersed in the fluid, a stream of air (20 liters/hr) is passed through the fluid. This test is conducted at a temperature of 500°F with a test duration of 24 hours. The stability of the fluid to decomposition is evaluated by measuring the changes in viscosity and acid number. The formation of solids in the fluid is observed. The loss of fluid from the sample tube is determined. The metal specimens are weighed and examined to determine the effect of the fluid on the various metals. The oxidation-corrosion test provides some of the elements of an engine's environment, i.e., high temperature, oxidation, and various metallic surfaces. Many other factors are not present, such as the high sliding speeds, loads, thin films of liquid lubricant, hot spots, and the proper ratios of lubricant volume to air flow, oxygen content, and surface areas of the engine components.

The "Micro" oxidation-corrosion test, therefore has no direct correlation with actual engine performance. The test is useful, however, for comparing the new fluids with other fluids on which some advanced data have been obtained. One of these fluids is 5-phenyl ether (5P4E), which has undergone tests in high temperature component rigs and engines. It is believed to be the only fluid, available in quantity, that has the necessary high temperature properties for a $500^{\circ}F$ engine oil. The major weakness of 5P4E is its poor low temperature fluidity. With a pour point of $+40^{\circ}F$, its use would require auxiliary heaters, or dilution with other fluids to permit engine start-up at low temperatures. Because of its demonstrated superior high temperature properties, the laboratory data on 5P4E is used as a reference for rating new high temperature materials. Table 1 shows oxidation-corrosion data obtained on the 5P4E (Base Fluid) and several new materials. Thus far, the only materials comparable with 5P4E under these conditions are the cyclic phosphonitriles. The preliminary samples of this class of compounds however have high pour points. To be considered for extensive testing in the simulated component rigs, a new fluid must be comparable, or better, than 5P4E in most of the laboratory studies listed in Figure 2, and show a significant improvement in low temperature properties over 5P4E.

The other fluid being used as a reference is MIL-L-9236 which also has been evaluated in high temperature components and advanced engines. It has a bulk oil temperature limit of $425^{\circ}F$. Candidate fluids that do not compare favorably with 5P4E at $500^{\circ}F$ are eventually compared with MIL-L-9236 at $425^{\circ}F$. Those base fluids that are comparable at $425^{\circ}F$ with MIL-L 9236 (Formulation) may be tested at $450^{\circ}F$ and $475^{\circ}F$ to determine upper limits and to indicate progress made toward the $500^{\circ}F$ goal.

As a supplement to oxidation-corrosion data, an oxidation test is also conducted on new fluids. In this test, the same procedures and apparatus are used as in oxidation-corrosion, however no metals are present. Table 2 shows both types of test results on an alkyl pyrazine compared with MIL-L-9236 formulation at $425^{\circ}F$. Included are data on the base fluid as well as the formulation. Generally, oxidation data show less degradation of the fluid than do the oxidation-corrosion data. Recent studies with certain fluids have shown the reverse to be true. The presence of the metals seemed to have a beneficial effect, as indicated by significantly reduced changes in viscosity and acid number.

Thermal stability tests are conducted to provide a measure of the degradation characteristics of the fluid under thermal stress, without the oxidative decomposition which occurs in the high temperature oxidation-corrosion test. A number of thermal stability tests for liquids are in use today. As a result, thermal stability means many things to many people. These tests range from thermal decomposition point as obtained by the isoteniscope or by differential thermal analysis, (DTA) to the bomb or open vessel tests under nitrogen which evaluate the changes in the fluid after exposure at various temperatures and times.

The isoteniscope and the DTA procedures provide information on the temperature at which decomposition is initiated, but do not reveal the effect of long-term thermal stress on the bulk fluid properties. The other tests, while showing bulk property changes do not indicate the initial decomposition point or the mechanisms by which the degradation proceeds.

At the present time, isoteniscope data are being used by the development group for initially comparing the thermal stabilities of candidate fluids. Considerable effort, however is underway and being planned for a study of existing methods as well as new methods to give (1) basic information on modes of thermal degradation and (2) information on bulk fluid property changes more closely related to the various applications in which a fluid will ultimately be used.

Traditional fluid properties such as viscosity, pour point, flash and fire are evaluated by the standard methods. Volatility at temperatures from 400°F to 500°F is determined by ASTM method D 972 for evaporation loss. The test duration, however is only 6 1/2 hours.

The anti-wear properties of base fluids and formulations containing antiwear additives are evaluated by means of the Shell Four Ball Test. Currently, data are obtained under various combinations of test conditions: Temperatures, 167°F and 400°F; Loads, 10 kg and 40 kg; speeds, 600 rpm and 1200 rpm; 4-Ball Material: 52100 and M-10.

The hydrolytic stability of the candidate fluids is determined by means of Federal Test Method Standard 791, Method 3457 T.

After characterization by most of the above procedures, the most promising base fluids are formulated with high temperature anti-oxidants and anti-wear additives. A number of new anti-oxidants developed by Monsanto Research Corporation, appear to be promising in polyphenyl ethers, and esters. Based on preliminary data, metal chelates, such as Nickel bis (N-phenyl 5 nitrosalicylamine) are of greatest interest. The formulations having the greatest improvement over the base fluid (on the basis of oxidation-corrosion) are further studied to determine optimum concentration of additives. At this point, the candidate formulations for large scale evaluation are selected.

The current status of liquid lubricants development contractually and in-house can be summarized as follows:

Advanced Gas Turbine Oils: Polyphenyl ether (5P4E) is the only fluid, on which considerable data have been obtained, which shows promise as a 500°F gas turbine oil. Some of the cyclic phosphonitriles appear to be similar to 5P4E on the basis of preliminary oxidation-corrosion tests. These materials, like the polyphenyl ethers must be improved from the standpoint of low temperature fluidity. In addition to structural modifications, blending studies with esters are being carried out on both classes of material to effect low temperature fluidity.

Hydraulic-Fluids: Super-refined deep dewaxed mineral oils, synthetic hydrocarbons, and chlorinated silicones are the most promising currently available advanced hydraulic fluid candidates. Some experimental alkyl pyrazine fluids are also being studied as high temperature hydraulic fluids.

Fluids For Lubricating Greases: High phenyl content methyl-phenyl silicones are the most promising candidates for use in greases operating at 600°F in bearing performance tests (Pope Spindles).

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FUTURE

The foregoing has presented the current program of initial property evaluation of new high temperature fluids. Most of the test procedures are extensions of tests used in the past under less severe conditions. As lubricant requirements advanced the test procudures were gradually modified to keep pace. This was accomplished primarily through the use of more severe test conditions rather than radical changes in concept. These procedures are, at best, rough screening tests when used to select promising fluids for a 500 ^{o}F gas turbine oil. They are primarily concerned with bulk properties of fluids, and as such do not provide adequate data under the increasingly more severe environments. In the case of oxidation-corrosion tests it is not only important to know the extent of degradation of the fluid, but also the mechanism by which degradation proceeds. Knowledge of how and why fluids degrade, can be of guidance in research for more stable molecular structures and in the selection of more effective additives.

Contractual and in-house programs to provide this type of information are currently in progress. A specific example is the mechanism study of the oxidative degradation of polyphenyl ethers being carried out under Contract AF 33(616)-7853. An in-house program has been initiated in which vapor phase chromatography and infrared spectroscopy are being studied as means of identifying decomposition products formed during oxidation-corrosion tests.

These, and other laboratory studies will be continued and expanded in an overall effort to increase knowledge of basic properties of fluids. However, in the case of gas turbine oils these laboratory studies in themselves will not predict which fluids will make the best 500^{o}F gas turbine oil. The use of 5P4E data at 500^{o}F as a bench mark will provide some measure of selectivity, but a more direct relationship will to be established between (a) fluid properties as determined on small quantities of material in the laboratory and (b) fluid property requirements as determined in an engine. This more direct relationship can be promoted by a much closer liaison than now exists between the Liquid Lubricants Development Group and the other elements shown in Figure 1. For example, in studies on engine oils, development personnel should examine fluids and hardware from the large scale component rigs and engine tests, with interpretation of results provided by engine test personnel. Similarly, hardware and research personnel should feel free to visit the laboratories at ASD for direct observation and discussion of bench tests.

If all personnel, from fluids researcher to hardware engineer, have a good understanding of the functions and objectives of all of the other groups, the way is clear for a knowledgeable exhange of information that can lead to laboratory data that is more meaningful.

In closing, it is hoped that this paper has provided a better undertstanding of the workbeing done in the Fuels and Lubricants Branch on new research samples of potential advanced liquid lubricants.

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REFERENNCES

1. Adams, H. W. ASD TDR 62-268, "High Temperature (-40 to +550°F ambient) Power Transmission Fluid", July 1962.

2. Adams, H. W. WADD TR 60-536, "High Temperature Lubricants For Advanced Gas Turbine", November 1960.

3. Monsanto Research Corporation, Contract AF 33(616)-7853 and Contract AF 33(657)-8893.

4. Dolle, R. E. Jr. ASD TDR 63-177 "Base Stock Characterization and Formulation Development for High Temperature Gas Turbine Lubricants", to be published, May 1963.

5. Pennsylvania State University, Contract AF 33(616)-7590.

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TABLE 1

MICRO-OXIDATION-CORROSION TEST

Temperature : 500°F
Air Flow: 20 l/hr

Sample Size: 20 ml
Test Duration: 24 hrs.

SAMPLE NO.	FLUID	POUR POINT	% CHANGE IN VISCOSITY @ 100°F	% CHANGE IN ACID NO.	% FLUID LOSS	APPEARANCE OF FLUID & EFFECT ON METALS*
ELO 62-29	5P4E (Base Fluid)	+40	+5.2	none	5.5	oil slightly darkened, no solids formed. No corrosion of metals, tarnish from light to moderate.
ELO 62-28	Cyclic Tri Phosphonitrile (Base Fluid)	+60	+14.4	none	2.1	similar to 5P4E
ELO 62-25	Cyclic Tri & Tetrameric Phosphonitrile (Base Fluid)	+25	+7.5	none	13.7	similar to 5P4E
ELO 62-39	Polyol Ester (Formulated)	-30**	+56	none	37.5	Oil Darkened, negligible solids formed. Metals, moderate to heavy tarnish.

* Metals: Aluminum, titanium, silver, tool steel, stainless steel

** Some crystals formed at 0°F

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TABLE 2

MICRO-OXIDATION-CORROSION TEST

Temperature: 425°F
Air Flow: 20 l/hr.

Sample Size: 20 ml
Test Duration: 24 hrs.

SAMPLE NO.	FLUID	POUR POINT °F	% CHANGE IN VISCOSITY @ 100°F	% CHANGE IN ACID NO.	% FLUID LOSS	APPEARANCE OF FLUID & EFFECT ON METALS*
ELO 62-82	MIL-L-9236 (Formulated)	-75	+13.1	+0.3	4.8	oil darkened, negligible solids formed. Metals: no corrosion to moderate tarnish
ELO 62-96	Alkyl Pyrazine (Formulated)	-90	+51.4	+0.6	5.2	oil darkened, heavy solids formation. Metals, light corrosion to heavy tarnish.
ELO 62-96	Alkyl pyrazine (Base Fluid)	-90	-	-	26.8	Charred badly, solid at room temp. (<u>no metals used</u>)
ELO 62-96	Alkyl pyrazine (Formulated)	-90	+20.3	+0.3	18.5	Darkened. Light solids formation (<u>no metals used</u>)

* Metal washers: Aluminum, titanium, silver, tool steel, stainless steel